

U. S. Patent No. 4,405,667 issued to Christensen et al appears to disclose a retortable pouch having a linear low density polyethylene heat seal layer, a second layer of a blend of linear low density polyethylene and propylene ethylene copolymer, optional third, fourth, and fifth layers of propylene ethylene copolymer, a sixth layer of an anhydride modified polypropylene, a seventh layer of nylon, an eighth layer of ethylene vinyl alcohol copolymer and a ninth layer of nylon.

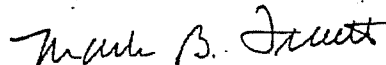
U. S. Patent No. 4,588,648 issued to Krueger et al appears to disclose a multiple layer plastic film having polypropylene adhered to nylon by an intermediate layer of a blend of an ungrafted propylene-based polymer and a graft copolymer of maleic anhydride onto an olefin polymer or copolymer, with additional layers of nylon, ethylene vinyl alcohol copolymer, and nylon.

By inclusion of any given document in this Information Disclosure Statement Applicant in no way admits that such document is effective as prior art against the above-identified application under either 35 USC section 102 or 35 USC section 103.

The Examiner is requested to independently review each of the cited references for their relevance to the present case.

Please charge any additional prosecutorial fees which may be due to Grace deposit account no. 07-1765.

Respectfully submitted,



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A04/861006/9/2



UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.

EXAMINER	
ART UNIT	PAPER NUMBER
	4

DATE MAILED: _____

EXAMINER INTERVIEW SUMMARY RECORD

All participants (applicant, applicant's representative, PTO personnel):

(1) Mark Quatt (3) _____

(2) _____ (4) _____

Date of interview Nov 4, 1986

Type: ☒ Telephonic ☐ Personal (copy is given to ☐ applicant ☐ applicant's representative).

Exhibit shown or demonstration conducted: ☐ Yes ☒ No. If yes, brief description: _____

Agreement ☒ was reached with respect to some or all of the claims in question. ☐ was not reached.

Claims discussed: all

Identification of prior art discussed: _____

Description of the general nature of what was agreed to if an agreement was reached, or any other comments:

Restriction:
I Claims 1-23, multilayer product, 428/426.3

I Claims 24-28 method of constructing
156-244.11 Applicant elected Group I Transverse.

(A fuller description, if necessary, and a copy of the amendments, if available, which the examiner agreed would render the claims allowable must be attached. Also, where no copy of the amendments which would render the claims allowable is available, a summary thereof must be attached.)

Unless the paragraphs below have been checked to indicate to the contrary, A FORMAL WRITTEN RESPONSE TO THE LAST OFFICE ACTION IS NOT WAIVED AND MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW (e.g., items 1-7 on the reverse side of this form). If a response to the last Office action has already been filed, then applicant is given one month from this interview date to provide a statement of the substance of the interview.

☒ It is not necessary for applicant to provide a separate record of the substance of the interview.

☐ Since the examiner's interview summary above (including any attachments) reflects a complete response to each of the objections, rejections and requirements that may be present in the last Office action, and since the claims are now allowable, this completed form is considered to fulfill the response requirements of the last Office action.

Thomas J. Hubert
Examiner's Signature

PTOL-413 (rev. 1-81)

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JB


UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office

 Address: COMMISSIONER OF PATENTS AND TRADEMARKS
 Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
06/842,600	03/21/86	SHAH	G 41257

 W. R. GRACE & CO.
 CRYOVAC DIVISION
 PATENT DEPT.
 P.O. BOX 464
 DUNCAN, SC 29334

EXAMINER	
HERBERT J. T.	
ART UNIT	PAPER NUMBER
154	5
DATE MAILED: 11/20/86	

This is a communication from the examiner in charge of your application.

COMMISSIONER OF PATENTS AND TRADEMARKS

☒ This application has been examined ☐ Responsive to communication filed on _____ ☐ This action is made final.

 A shortened statutory period for response to this action is set to expire 3 month(s), _____ day(s) from the date of this letter.
 Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133

Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:

- | | |
|---|---|
| 1. <input checked="" type="checkbox"/> Notice of References Cited by Examiner, PTO-892. | 2. <input checked="" type="checkbox"/> Notice re Patent Drawing, PTO-848. |
| 3. <input type="checkbox"/> Notice of Art Cited by Applicant, PTO-1449 | 4. <input type="checkbox"/> Notice of Informal Patent Application, Form PTO-152 |
| 5. <input checked="" type="checkbox"/> Information on How to Effect Drawing Changes, PTO-1474 | 6. <input type="checkbox"/> _____ |

Part II SUMMARY OF ACTION

1. ☒ Claims 1-28 are pending in the application.
 Of the above, claims 24-28 are withdrawn from consideration.
2. ☐ Claims _____ have been cancelled.
3. ☐ Claims _____ are allowed.
4. ☒ Claims 1-23 are rejected.
5. ☐ Claims _____ are objected to.
6. ☒ Claims 1-28 are subject to restriction or election requirement.
7. ☒ This application has been filed with informal drawings which are acceptable for examination purposes until such time as allowable subject matter is indicated.
8. ☐ Allowable subject matter having been indicated, formal drawings are required in response to this Office action.
9. ☐ The corrected or substitute drawings have been received on _____. These drawings are ☐ acceptable;
☐ not acceptable (see explanation).
10. ☐ The ☐ proposed drawing correction and/or the ☐ proposed additional or substitute sheet(s) of drawings, filed on _____, has (have) been ☐ approved by the examiner. ☐ disapproved by the examiner (see explanation).
11. ☐ The proposed drawing correction, filed _____, has been ☐ approved. ☐ disapproved (see explanation). However, the Patent and Trademark Office no longer makes drawing changes. It is now applicant's responsibility to ensure that the drawings are corrected. Corrections **MUST** be effected in accordance with the instructions set forth on the attached letter "INFORMATION ON HOW TO EFFECT DRAWING CHANGES", PTO-1474.
12. ☐ Acknowledgment is made of the claim for priority under 35 U.S.C. 119. The certified copy has ☐ been received ☐ not been received
☐ been filed in parent application, serial no. _____; filed on _____.
13. ☐ Since this application appears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.
14. ☐ Other

PTOL-326 (Rev. 7-82)

EXAMINER'S ACTION

Serial No. 842,600

-2-

Art Unit 154

15.

Restriction to one of the following inventions is required under 35 U.S.C. 121:

I. Claims 1-23, drawn to a multilayer article, classified in Class 428, subclass 476.3.

II. Claims 24-28, drawn to a method of coextruding, classified in Class 156, subclass 244.11.

16.

The inventions are distinct, each from the other, because of the following reasons:

Inventions II and I are related as process of making and product made.

The inventions are distinct if either (1) the process as claimed can be used to make another and materially different product, or (2) the product as claimed can be made by another and materially different process. MPEP 806.05(f).

In this case, the product as claimed can be made by a materially different process such as by laminating pre-formed layers together.

17.

Because these inventions are distinct for the reasons given above and have acquired a separate status in the art as shown by their different classification, restriction for examination purposes as indicated is proper.

18.

During a telephone conversation with applicant's attorney, Mr. Mark Quatt on November 5, 1986 a

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Art Unit 154

provisional election was made with traverse to prosecute the invention of Group I, claims 1-23. Affirmation of this election must be made by applicant in responding to this Office action. Claims 24-28 are withdrawn from further consideration by the examiner as being drawn to a nonelected invention. See 37 CFR 1.142(b).

19.

The following is a quotation of 35 U.S.C. 103 which forms the basis for all obviousness rejections set forth in this Office action:

A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Subject matter developed by another person, which qualifies as prior art only under subsection (f) and (g) of section 102 of this title, shall not preclude patentability under this section where the subject matter and the claimed invention were, at the time the invention was made, owned by the same person or subject to an obligation of assignment to the same person.

20.

Claims 1-23 are rejected under 35 U.S.C. 103 as being unpatentable over Sheptak or Hirt in view of Mueller.

Each of Sheptak and Hirt discloses a multilayered film comprising EVOH core with intermediate polyamide (e.g. nylon layers which in turn carry out polymeric

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Art Unit 154

layers such as polyolefin blends as shown in Sheptak. With Mueller further showing multilayered film structures having outer layers of polyolefin blends, e.g. LLDPE with LMDPE, ethylene/propylene copolymer, etc, it would be obvious to employ these outer layers of Mueller as the outer layers in Sheptak or Hirt.

21.

Knott et al., Rosenthal et al., Christensen et al., Theisen et al., Newsome, Farrell et al., Ohya et al., Super et al., Kaschak et al., Schoenberg and Newsome et al. -cited by applicant- are made of record as of interest. Note pages 2-4 of the specification and information statement by applicant' July 3, 1986.

TJHerbert:bh

(703) 557-6525

11/18/86



THOMAS J. HERBERT
PRIMARY EXAMINER
ART UNIT 154

PTO - 948
(Rev. 8-82)U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

ATTACHMENT TO PAPER NUMBER	5
S.N.	842600

GROUP 154

NOTICE OF PATENT DRAWINGS OBJECTION

Drawing Corrections and/or new drawings may only be submitted in the manner set forth in the attached letter, "Information on How to Effect Drawing Changes" PTO-1474.

A. ☒ The drawings, filed on 3/21/86, are objected to as informal for reason(s) checked below:

- | | |
|--|--|
| 1. <input type="checkbox"/> Lines Pale. | 11. <input type="checkbox"/> Parts in Section Must Be Hatched. |
| 2. <input type="checkbox"/> Paper Poor. | 12. <input type="checkbox"/> Solid Black Objectionable. |
| 3. <input checked="" type="checkbox"/> Numerals Poor.
<i>Pencil Dig</i> | 13. <input type="checkbox"/> Figure Legends Placed Incorrectly. |
| 4. <input type="checkbox"/> Lines Rough and Blurred. | 14. <input type="checkbox"/> Mounted Photographs. |
| 5. <input type="checkbox"/> Shade Lines Required. | 15. <input type="checkbox"/> Extraneous Matter Objectionable.
[37 CFR 1.84 (1)] |
| 6. <input type="checkbox"/> Figures Must be Numbered. | 16. <input checked="" type="checkbox"/> Paper Undersized; either 8 1/2" x 14",
or 21.0 cm. x 29.7 cm. required. |
| 7. <input type="checkbox"/> Heading Space Required. | 17. <input type="checkbox"/> Proper A4 Margins Required:
<input type="checkbox"/> TOP 2.5 cm. <input type="checkbox"/> RIGHT 1.5 cm.
<input type="checkbox"/> LEFT 2.5 cm. <input type="checkbox"/> BOTTOM 1.0 cm. |
| 8. <input type="checkbox"/> Figures Must Not be Connected. | 18. <input checked="" type="checkbox"/> Other:
<i>pen & ink dug red</i> |
| 9. <input type="checkbox"/> Criss-Cross Hatching Objectionable. | |
| 10. <input type="checkbox"/> Double-Line Hatching Objectionable. | |

B. ☒ The drawings, submitted on 3/21/86, are so informal they cannot be corrected. New drawings are required. Submission of the new drawings MUST be made in accordance with the attached letter.

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

Attachment to Paper Number	5
Serial No.	842,600

INFORMATION ON HOW TO EFFECT DRAWING CHANGES

1. Correction of Informalities (Draftsman's objections on PTO-948)

In order to correct any informalities in the drawings, applicants MUST comply with options (a) or (b) below. Failure to do so will result in ABANDONMENT of the application.

a) File new drawings with the changes incorporated therein. Applicant may delay filing of the new drawings until the application is allowed by the examiner. If delayed, the new drawings MUST be filed within the THREE MONTH statutory period set for payment of the base issue fee in the "NOTICE OF ALLOWANCE AND BASE ISSUE FEE DUE" (PTOL-85). Also, if delayed, the drawings should be filed as a separate paper with a transmittal letter addressed to the Official Draftsman and which indicates the following in the upper right hand corner:

Date of the Notice of Allowance
Issue Batch Number
Serial Number

b) Request a commercial bonded drafting firm (see list below) to make the necessary corrections.

A BONDED DRAFTSMAN MUST BE AUTHORIZED, THE CORRECTIONS EXECUTED AND THE CORRECTED DRAWINGS RETURNED TO THE OFFICE DURING THE THREE MONTH STATUTORY PERIOD SET FOR PAYMENT OF THE BASE ISSUE FEE IN THE "NOTICE OF ALLOWANCE AND BASE ISSUE FEE DUE" (PTOL-85). NOTE THAT THE STATUTE DOES NOT PERMIT EXTENSION OF THE THREE MONTH PERIOD SET TO PAY THE BASE ISSUE FEE.

2. Corrections other than Informalities Noted by the Draftsman on the PTO-948.

All changes to the drawings, other than informalities noted by the Draftsman, MUST be made in the same manner as above except that, if delayed option (a) is selected, normally, a sketch of the changes to be incorporated into the new drawings MUST be approved by the examiner before the application will be allowed. If option (b) is selected, normally, applicants must submit, in duplicate, a separate paper containing a sketch of the proposed changes before the application will be allowed. No changes will be permitted to be made, other than correction of informalities, unless the examiner has approved the proposed changes.

3. Listing of Bonded Draftsmen

SEE LIST ON REVERSE SIDE OF THIS FORM.

IT IS SUGGESTED THAT APPLICANTS DETACH THIS LETTER FROM THE OFFICE ACTION AND ATTACH IT TO THE FRONT OF APPLICANT'S FILE AS A REMINDER THAT, IN ORDER TO AVOID ABANDONMENT, A BONDED DRAFTSMAN MUST BE AUTHORIZED, THE CORRECTIONS EXECUTED AND THE CORRECTED DRAWINGS RETURNED TO THE OFFICE, OR NEW DRAWINGS SUBMITTED, DURING THE THREE MONTH STATUTORY PERIOD SET FOR PAYMENT OF THE BASE ISSUE FEE. NOTE THAT THE STATUTE DOES NOT PERMIT EXTENSION OF THE THREE MONTH PERIOD SET TO PAY THE BASE ISSUE FEE.

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TO SEPARATE OLD TOP AND BOTTOM EDGES, SNAP-APART AND DISCARD CARBON

FORM PTO-892 (REV. 3-78)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		SERIAL NO. 842,600	GROUP/UNIT 1574	ATTACHMENT TO PAPER NUMBER 5		
NOTICE OF REFERENCES CITED				APPLICANT(S) Shah				
U.S. PATENT DOCUMENTS								
*	DOCUMENT NO.	DATE	NAME	CLASS	SUB-CLASS	FILING DATE IF APPROPRIATE		
✓A	4182457	1-1980	Yamada et al.	428	3542			
✓B	4405667	9-1983	Christensen et al.	428	35			
✓C	4561920	12-1985	Foster	156	24411			
✓D	4588648	5-1986	Krueger et al.	428	475.8	9/20/84		
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FOREIGN PATENT DOCUMENTS								
*	DOCUMENT NO.	DATE	COUNTRY	NAME	CLASS	SUB-CLASS	PERTINENT SHTS. DWG.	PP SPEC.
L								
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Q								
OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)								
R								
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U								
EXAMINER J. Herbert Jr.				DATE 6/8/87				
* A copy of this reference is not being furnished with this office action. (See Manual of Patent Examining Procedure, section 707.05 (a).)								

United States Patent [19][11] **4,182,457**

Yamada et al.

[45] **Jan. 8, 1980**[54] **MULTILAYER CONTAINER**

[75] **Inventors:** Masaki Yamada, Ebina; Sadao Hirata, Yokohama; Jinichi Yuzaki, Tokyo; Yoshitsugu Marubashi, Yokohama; Kazuhiko Sakano, Tokyo; Akira Kishimoto; Shunsuke Hirata, both of Yokohama; Toru Suzuki, Yokosuka; Fumio Kano, Kamakura, all of Japan

[73] **Assignee:** Toyo Soda Kaisha Limited, Tokyo, Japan

[21] **Appl. No.:** 821,484

[22] **Filed:** Aug. 3, 1977

[30] **Foreign Application Priority Data**

Aug. 10, 1976 [JP] Japan 51-94533
Jul. 18, 1977 [JP] Japan 52-45114

[51] **Int. Cl.** B32B 15/08; B32B 27/08

[52] **U.S. Cl.** 215/1 C; 220/453; 229/1.5 B; 426/127; 428/35

[58] **Field of Search** 428/35, 340, 474, 910; 215/1 C; 156/243, 244.11, 244.14, 244.22; 229/1.5; 106/324.1, 524.2, 524.3, 524.4, 524.5, 524.6, 524.7, 524.8; 220/453; 426/106, 126, 127, 129, 415

[56] **References Cited****U.S. PATENT DOCUMENTS**

Re. 29,340	8/1977	Matsunari et al.	428/474
3,630,826	12/1977	Rose et al.	426/127
3,908,070	9/1975	Marzoff	428/474
3,949,114	4/1976	Viola et al.	428/474
4,058,647	11/1977	Inoue et al.	426/127

Primary Examiner—Caleb Weston

Attorney, Agent, or Firm—Diller, Ramik & Wight

[57] **ABSTRACT**

A transparent multi-layer container comprising a co-extrudate of an oxygen-barrier resin layer and an orienting resin layer which is monoaxially or biaxially oriented is disclosed. An adhesive resin layer is preferably interposed between the oxygen-barrier layer and the orienting resin layer, and this co-extrudate is drawn and molded at a specific temperature determined relatively to the melting points and softening points of the respective resins. This container is excellent in the combination of transparency, rigidity, mechanical strength, gas-barrier property and interlaminar peel strength.

9 Claims, No Drawings

4,182,457

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MULTILAYER CONTAINER

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention relates to a multi-layer plastic drawn and molded container excellent in transparency, rigidity, mechanical strength, water resistance and gas barrier property to oxygen and the like and having a practically satisfactory interlaminar peel strength under falling, shaking or impact, and to a process for the preparation of this excellent container.

(2) Description of the Prior Arts

It is well known that when a thermoplastic resin is drawn at a relatively low temperature, namely at a temperature lower than the melting point or softening point of the resin or a temperature just above the melting point or softening point of the resin, as a result of orientation of the polymer chain or crystal, such properties as rigidity, mechanical strength, gas barrier property and transparency can be improved. These improvements are practically utilized in biaxially drawn films, filaments, drawn tapes, biaxially drawn blow bottles and draw-molded cups.

In the field of narrow- and broad-mouthed hollow plastic containers, for example, a biaxially drawn blow bottle of the vinylidene chloride resin type molded according to the method disclosed in Japanese Pat. Publication No. 8583/63 has heretofore been broadly used as a ketchup bottle because it has an excellent gas barrier property. However, because of generation of poisonous gases on burning or migration of the monomer or additive into the content, bottles of this type are hardly used at the present. Biaxially drawn blow bottles of polypropylene formed according to the principle, method and apparatus disclosed in Japanese Pat. Publication No. 16245/63, Japanese Patent Application Laid-Open Specification No. 3492/71, etc., have excellent transparency, rigidity and mechanical strength, and they are broadly used as bottles for shampoo or the like instead of polyvinyl chloride bottles in U.S.A. and as bottles for medicines, for example, Ringer's solution, instead of glass bottles in Japan. Further, broad-mouthed polypropylene cups prepared by solid-phase pressure forming at a relatively low temperature according to the method disclosed in Kunststoffe Bd. 65, 1975, H. 10, page 666 have now been attracting attentions as substitutes for polyvinyl chloride cups. Further, biaxially drawn blow bottles of polyethylene terephthalate disclosed in the specification of U.S. Pat. No. 3,733,309 have been test-marketed as bottles for carbonated drinks and now attract attentions in the art.

In case of the above-mentioned biaxially drawn blow bottles of the vinylidene chloride resin type, when a contained liquid, semi-liquid or pasty food has contact with the inner wall of the bottom, a problem of migration of the monomer or the like rises, and they cannot be regarded as practical semi-rigid containers. Biaxially drawn blow bottles of polypropylene and polypropylene cups prepared by solid phase pressure forming are inferior in the gas barrier property, and they cannot substantially be applied to foods of which the preservability is sensitive to oxygen permeating through the container wall. Although biaxially drawn blow bottles of polyethylene terephthalate have a relatively high gas barrier property and are very excellent in rigidity and transparency, when they are allowed to stand in an atmosphere maintained at 60° to 70° C. for 3 to 5 min-

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utes, they show such thermal shrinkage as an empty volume shrinkage of 1 to 3%, a total height shrinkage of 0.4 to 0.8% and a barrel diameter shrinkage of 0.7 to 1.2%. Further, when they are allowed to stand in an atmosphere maintained at 80° C. for 1 minute, they are deformed to such an extent that they cannot be practically used. Accordingly, these bottles cannot be used when hot filling of contents is conducted or for storage of foods requiring heat sterilization, for example, sauces.

For the foregoing reasons, as in case of melt-molded containers, multi-layer structures in which defects of respective resins are compensated and which can meet practical demands are required in case of not only biaxially drawn blow molded containers prepared by forming a thermoplastic resin into a bottomed or bottomless parison and conducting the step of elongating the parison in the axial direction thereof at a relatively low temperature, for example, the melting point of the resin and the step of inflating the parison in a direction rectangular to the axial direction simultaneously or in this order (namely in sequence) but also biaxially drawn cups pressure-formed in the solid phase from a sheet at a relatively low temperature.

Drawn multi-layer containers are proposed in, for example, the specification of U.S. Pat. No. 3,733,309 and Japanese Patent Application Laid-Open Specification No. 32164/73, but these known drawn multi-layer containers are still insufficient from the practical viewpoint with respect to the interlaminar strength between every two adjacent layers, selection of constituent resin layers and selection of molding conditions such as the molding temperature and draw ratio. In addition, use of an unsaturated carboxylic acid-grafted thermoplastic resin as an adhesive improving the interlaminar peel strength has been proposed in, for example, Japanese Patent Application Laid-Open Specification No. 67384/76, but in this proposal, no sufficient regard is paid to the relation between the molding conditions such as the molding temperature and draw ratio and the adhesiveness.

BRIEF SUMMARY OF THE INVENTION

We found that in order to obtain biaxially drawn blow-molded bottles or draw-molded containers such as solid phase pressure-formed cups, which have a high barrier property to gases such as oxygen and are excellent in the combination of transparency, rigidity, mechanical strength and other physical properties, it is necessary to select very strictly constituent resin layers and molding conditions such as the molding temperature and draw ratio in view of the practical utility and moldability.

We also found that when a draw-molded container is prepared from a multi-layer structure comprising an oxygen-barrier thermoplastic resin layer and a layer of an orienting thermoplastic resin other than the oxygen-barrier thermoplastic resin preferably with an adhesive resin layer interposed between said two resin layers, in order to attain a high interlaminar peel strength, it is very important to select the respective resins so that a specific relation is established among the melting or softening points of the resins and to perform draw-molding at a temperature in a specific range.

In accordance with the present invention, there is provided a container having a multi-layer structure, which comprises a plurality of thermoplastic resins,

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wherein at least one layer of the container is composed of an oxygen-barrier thermoplastic resin having an oxygen permeability lower than 5.5×10^{-12} cc-cm/cm²-sec-cmHg as measured at 37° C. and at least one of the remaining layers comprises an orienting thermoplastic resin other than the oxygen-barrier thermoplastic resin, said two resins are selected so that the requirement represented by the following formula:

$$|T_g - T_0| \leq 35^\circ \text{C.}$$

wherein T_g stands for the melting or softening point (°C.) of said oxygen-barrier thermoplastic resin and T_0 stands for the melting or softening point (°C.) of said orienting thermoplastic resin,

is satisfied, and wherein at least one of two-dimensional orientation coefficients (l and m) of at least one layer composed of said orienting thermoplastic resin in a smallest-thickness portion of the container is at least 0.05.

In accordance with the present invention, there is also provided a container having a multi-layer structure, which comprises at least one layer composed of an oxygen-barrier thermoplastic resin having an oxygen permeability lower than 5.5×10^{-12} cc-cm/cm²-sec-cmHg as measured at 37° C., at least one layer comprising an orienting thermoplastic resin other than the oxygen-barrier thermoplastic resin and at least one layer interposed between said oxygen-barrier thermoplastic resin layer and said orienting thermoplastic resin layer and being composed of a resin having an adhesiveness to both of said resins, wherein said three resins are selected so that the requirements represented by the following formulae:

$$|T_g - T_0| \leq 35^\circ \text{C.}$$

and

$$90^\circ \text{C.} \geq T_0 - T_c \geq 7^\circ \text{C.}$$

wherein T_g stands for the melting or softening point (°C.) of said oxygen-barrier thermoplastic resin, T_0 stands for the melting or softening point (°C.) of the melting or softening point of said orienting thermoplastic resin and T_c stands for the melting or softening point (°C.) of said adhesive resin, at least one of two-dimensional orientation coefficients (l and m) of at least one layer composed of said orienting thermoplastic resin in a smallest-thickness portion of the container is at least 0.05, and wherein the layer of said adhesive resin is substantially non-oriented.

This invention will now be described in detail.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS Resin Components

In the container of this invention, in order to attain the foregoing objects, it is important that a gas-barrier resin having an oxygen permeability lower than 5.5×10^{-12} cc-cm/cm²-sec-cmHg as measured at 37° C. and an orienting thermoplastic resin other than the gas-barrier resin should be selected and combined as the layer-constituting resin so that the difference ($\Delta t = |T_g - T_0|$) between the melting or softening point (T_g) of the gas-barrier resin and the melting or softening point (T_0) of the orienting thermoplastic resin is smaller than 35° C., especially smaller than 10° C.

In the instant specification and appended claims, the melting point is defined as the thermodynamic primary

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transition point at which the crystal phase of a crystalline or semi-crystalline polymer is molten, as described in "Crystallization of Polymers" written by Leo Mandelkern and published by McGraw-Hill Book Company in 1964, and in general, the melting point can easily be determined according to the differential thermal analysis method, the specific heat-temperature curve method, the polarizing microscope method, the X-ray diffraction method, the infrared absorption spectrum method or the like.

Further, in the instant specification and appended claims, the softening point corresponds to the thermodynamic secondary transition point, i.e., the glass transition point, at which a polymer is substantially softened. This softening point is described in, for example, "Physics of Polymers" compiled by Japanese Association of Physics and published by Asakura Shoten in 1963 and can easily be determined by the specific heat- or specific volume-temperature curve method, the differential thermal analysis method or the industrial test methods such as methods of ASTM D 648-56, ASTM D 1525-58T and ASTM D 569-48.

In general, melt-extrudable thermoplastic resins having a good gas-barrier property to gases such as oxygen and carbon dioxide gas, for example, ethylene-vinyl alcohol copolymers and nylon resins, contain polar groups such as hydroxyl groups and amide groups on the main or side chains of polymers. The melting or softening points of these resins vary broadly depending on the content of polar groups, the chemical composition and other factors.

As described in the specifications of U.S. Pat. Nos. 3,183,203 and 3,419,654, ethylene-vinyl alcohol copolymers can be obtained by saponifying a copolymer of ethylene or a combination of the majority of ethylene and the minority of other olefins such as propylene with a vinyl ester of a lower fatty acid such as vinyl formate, vinyl acetate, vinyl propionate or the like, especially an ethylene-vinyl acetate copolymer. It has been found that in ethylene-vinyl alcohol copolymer resins, the following relation is substantially established between the melting point (T_m) determined according to the differential thermal analysis method or the like and the mole content (%) of ethylene:

$$T_m = 1.64X + 64$$

(3)

wherein T_m stands for the melting point of an ethylene-vinyl alcohol copolymer having an ethylene content of 0 to 80 mole % and X stands for the vinyl alcohol content (mole %) in the copolymer.

It has also been found that in case of nylons of the ring opening polymerization type the melting point varies depending on the kind of the amino acid monomer, in case of nylons of the polycondensation type the melting point varies depending on the kind of the acid and the amine, in case of nylons of the copolymer type the melting point varies depending on the monomer composition, and that in case of nylon polymer blends the melting point varies depending on the polymer blending ratio. Melting points of these nylon type polymers as determined according to the differential thermal analysis method or the like are as shown in Table I given hereinafter.

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Table 1

Melting Points of Polyamide Resins	
Resin	Melting Point (T _m), °C.
Polyamides of Ring Opening Polymerization Type	
<i>ω</i> -Aminocaproic acid polymer (nylon 6)	223
<i>ω</i> -Aminoheptanoic acid polymer (nylon 7)	213
<i>ω</i> -Aminooctanoic acid polymer (polymer 8)	200
<i>ω</i> -Aminononanoic acid polymer (nylon 9)	210
<i>ω</i> -Aminodecanoic acid polymer (nylon 10)	188
<i>ω</i> -Aminoundecanoic acid polymer (nylon 11)	185
<i>ω</i> -Aminododecanoic acid polymer (nylon 12)	180
<i>ω</i> -Aminotridecanoic acid polymer (nylon 13)	180
Polyamides of Polycondensation Type	
Polyhexamethylene adipamide (6,6-nylon)	265
Polyhexamethylene azelamide (6,9-nylon)	185
Polyhexamethylene sebacamide (6,1-nylon)	225
Polyhexamethylene dodecamide (6,12-nylon)	212
Polyhexamethylene tridecamide (6,13-nylon)	204
Polydodecamethylene hexamide (10,6-nylon)	225
Polydodecamethylene sebacamide (10,10-nylon)	213
Polydodecamethylene dodecamide (10,12-nylon)	195
Polydodecamethylene tridecamide (10,13-nylon)	187
Polydodecamethylene adipamide (12,6-nylon)	210
Polydodecamethylene sebacamide (12,10-nylon)	190
Polydodecamethylene dodecamide (12,12-nylon)	185
Polytridecamethylene sebacamide (13,10-nylon)	170
Polytridecamethylene tridecamide (13,13-nylon)	174
Nyloes of Copolymer Type	
6,6-Nylon-6,10-Nylon Copolymer	
6,6-nylon content of 0 mole %	223
6,6-nylon content of 20 mole %	202
6,6-nylon content of 30 mole %	192
6,6-nylon content of 40 mole %	195
6,6-nylon content of 60 mole %	210
6,6-nylon content of 80 mole %	213
6,6-nylon content of 100 mole %	265
6-Nylon-6,6-Nylon Copolymers	
6,6-nylon content of 0 mole %	223
6,6-nylon content of 20 mole %	163
6,6-nylon content of 40 mole %	156
6,6-nylon content of 60 mole %	170
6,6-nylon content of 80 mole %	220
6,6-nylon content of 100 mole %	265
Nylon Polymer Blends	
6-Nylon-6,6-Nylon Blends	
6,6-nylon mixing ratio of 0%	223
6,6-nylon mixing ratio of 20 mole %	215
6,6-nylon mixing ratio of 40 mole %	210
6,6-nylon mixing ratio of 60 mole %	248
6,6-nylon mixing ratio of 80 mole %	250
6,6-nylon mixing ratio of 100 mole %	265

As pointed out hereinbefore, in resins having a barrier property to a gas such as oxygen, for example, ethylene-vinyl alcohol copolymers and nylon resins, the melting or softening point varies depending on the content of a polar group such as a hydroxyl or amide group or the chemical composition.

Data of the oxygen permeability (PO₂, cc-cm/cm²-sec-cmHg) as determined at 37° C. in the absolute dry state of ethylene-vinyl alcohol copolymers and polyamides excellent in the barrier property to gases such as oxygen are shown in Table 2 given hereinafter.

Table 2

Oxygen Permeabilities of High Gas-Barrier Resins	
Resin	PO ₂ × 10 ¹² cc-cm/cm ² -sec-cmHg (at 37° C. and 0% RH)
Ethylene-Vinyl Alcohol Copolymers	
Vinyl alcohol content of 40 mole %	1.8
Vinyl alcohol content of 50 mole %	0.5
Vinyl alcohol content of 60 mole %	0.1

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Table 2-continued

Oxygen Permeabilities of High Gas-Barrier Resins	
Resin	PO ₂ × 10 ¹² cc-cm/cm ² -sec-cmHg (at 37° C. and 0% RH)
Vinyl alcohol content of 70 mole %	0.07
Vinyl alcohol content of 80 mole %	0.04
Polyamides	
6-Nylon	4.0
10-Nylon	4.5
11-Nylon	4.9
12-Nylon	5.3
6,6-Nylon	0.69
6,10-Nylon	0.8
10,6-Nylon	0.81
6-Nylon-6,6-nylon copolymer (6-nylon content = 10 mole %)	1.0
6-Nylon-6,6-nylon copolymer (6-nylon content = 30 mole %)	2.0

20 In this invention, use of a thermoplastic resin having an oxygen permeability (PO₂) lower than 4.5 × 10⁻¹² cc-cm/cm²-sec-cmHg as determined at 37° C. is preferred, and an ethylene-vinyl alcohol copolymer, especially a saponified ethylene-vinyl acetate copolymer having an ethylene content of 25 to 65 mole % and a degree of saponification of at least 99 mole %, is most preferred. Of course, nylon resins can also be used conveniently. These oxygen-barrier thermoplastic resins should, of course, have a molecular weight sufficient to form a film.

25 In this invention, in order to obtain a container comprising an oxygen-barrier resin layer (A) and an orienting resin layer (B), in which the orienting resin layer is effectively oriented and the adhesiveness between the two resin layers and the transparency as a whole are excellent, the two resins should be selected so that their melting or softening points satisfy the requirement represented by the above formula (1).

30 In general, when a parison or sheet having a multi-layer structure is subjected to draw molding or solid phase pressure forming, the interlaminar peel strength between two layers is drastically reduced. It is believed that the reason for reduction of the interlaminar peel strength is that the respective layers show different responses deformation caused from the outside and a force given from the outside, namely they differ from each other in viscoelastic characteristics, unless the layer-constituting resins are thermoplastic resins having quite the same chemical and physical properties and therefore, different stresses or strains are caused in interfaces between every two adjacent layers, resulting in reduction of the adhesive force. This undesirable phenomenon is often observed also in the case where an unsaturated carboxylic acid-modified thermoplastic resin is used as an adhesive layer between a layer of a versatile resin such as polyolefin and a layer of a high gas-barrier resin such as mentioned above.

35 We found that when a parison or sheet having a multi-layer structure is molded into a container, in order to enhance the transparency and interlaminar peel strength, it is important that a high oxygen-barrier resin such as mentioned above and an orienting resin such as mentioned above should be selected so that the difference (ΔT) between the melting or softening point (T_g) of the high oxygen-barrier resin and the melting or softening point (T_o) of the orienting resin is not larger than 35° C., and that at least one of two-dimensional orientation coefficients (l and m) of at least one layer of the

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orienting resin in a smallest-thickness portion of the final molded container should be at least 0.05.

More specifically, it was found that when the melting or softening point (T_B) of the high barrier resin is lower than the melting or softening point (T_O) of the orienting resin by more than 35° C., under container-molding conditions giving the above-mentioned degree of orientation, the high barrier resin is in the completely molten state and because of extreme thickness unevenness of the high barrier resin layer caused in response to the temperature distribution of the parison or sheet at the molding step or of heat generation caused by solidification or crystallization of the high barrier resin at the cooling stage after the molding step, the orientation and transparency of the orienting resin layer other than the high barrier resin layer are drastically reduced. Moreover, it was found that when the melting or softening point (T_B) of the high barrier resin is higher than the melting or softening point (T_O) of the orienting resin by more than 35° C., under molding conditions giving the above-mentioned degree of orientation, the high barrier resin is in the relatively viscoelastically solid state and a high stress is generated on the interface between the high barrier resin layer and the adjacent other resin layer, to cause drastic reduction of the interlaminar peel strength in the final molded container. As will be apparent from these findings, it is especially important that the high oxygen-barrier resin and orienting resin should be selected so that the difference (Δt) between the melting or softening point (T_B) of the high oxygen-barrier resin and the melting or softening point (T_O) of the orienting resin is not larger than 35° C.

As the orienting thermoplastic resin (B), any of known thermoplastic resins capable of being oriented by drawing, other than the above-mentioned oxygen-barrier thermoplastic resin (A), can be used in this invention, so far as the above-mentioned requirements are satisfied. For example, homopolymers of olefins represented by the following formula:



wherein R stands for a hydrogen atom or an alkyl group having up to 4 carbon atoms, such as ethylene, propylene, butene-1, pentene-1 and 4-methylpentene-1, copolymers of these olefins, copolymers of these olefins with a small amount, generally 0.05 to 10% by weight based on the olefin, of other ethylenically unsaturated monomer such as vinyl acetate, an acrylic acid ester or the like, and blends of two or more of the foregoing polymers can be preferably employed for production of multi-layer parisons or sheets to be used in this invention, so far as they are crystalline. In order to obtain a molded container excellent in the rigidity and mechanical strength by draw molding, it is very important that homopolymers or copolymers of olefins should be crystalline. As the olefin homopolymer or copolymer, crystalline polypropylene is most preferred in view of the transparency and mechanical properties. In addition, there can be mentioned an ethylenepropylene copolymer, high density polyethylene, poly-4-methylpentene-1, polybutene-1 and medium density polyethylene in an order of importance. As the ethylenepropylene copolymer, a crystalline polymer comprising 0.5 to 15 mole % of ethylene and 85 to 95.5 mole % of propylene is especially valuable. In general, the olefin homopolymer or copolymer to be used should have a molecular weight

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sufficient to form a film, and it is preferred that the melt index (as determined according to the method of ASTM D-1238) of the olefin homopolymer or copolymer be 0.0001 to 5, especially 0.01 to 2.5.

Another instances of the orienting thermoplastic resin include polycarbonates and thermoplastic acrylic resins. As preferred examples of the polycarbonate, there can be mentioned polymers of carbonic acid esters obtained by reaction of bisphenol with phosgene, and as preferred examples of the acrylic resin, there can be mentioned homopolymers and copolymers of acrylic acid esters and methacrylic acid esters.

In this invention, the orienting resin layer may be a layer of a blend of the orienting thermoplastic resin with other thermoplastic resin, for example, the above-mentioned oxygen-barrier resin or an adhesive resin described hereinafter, so far as the orienting thermoplastic resin is a main component. If this feature is adopted, flashes formed at the step of molding of containers can be used for formation of the orienting resin layers.

In this invention, it is preferred that the oxygen-barrier thermoplastic resin (A) and the orienting thermoplastic resin (B) be selected and combined so that the requirement represented by the following formula:

$$0.617T_O - 54.8 \leq X \leq 0.617T_O - 26.2 \quad (5)$$

wherein T_O stands for the melting or softening point (°C.) of the orienting thermoplastic resin (B) and X stands for the content (mole %) of the vinyl alcohol units in the oxygen-barrier thermoplastic resin (A), is satisfied.

In this invention, in general, it is preferred that an adhesive resin (C) having an adhesiveness to both the oxygen-barrier thermoplastic resin layer (A) and the orienting thermoplastic resin layer (B) be interposed between the two layers (A) and (B).

Any of known resins having an adhesiveness to the above-mentioned oxygen-barrier thermoplastic resin (A) and orienting thermoplastic resin (B) can be used as the adhesive resin (C). In general, however, as the adhesive polymer (C), there are employed thermoplastic polymers having carbonyl groups



derived from functional groups of free carboxylic acids, carboxylic acid salts, carboxylic acid esters, carboxylic acid amides, carboxylic anhydrides, carbonic acid esters, urethane, urea or the like. In these thermoplastic polymers, the carbonyl group concentration may be changed in a broad range, but in general, it is preferred to use a thermoplastic polymer containing carbonyl groups at a concentration of 10 to 1400 millimoles per 100 g of the polymer, especially 30 to 1200 millimoles per 100 g of the polymer. Preferred adhesive resins include polyolefins modified with at least one ethylenically unsaturated monomer selected from unsaturated carboxylic acids and anhydrides, esters and amides thereof, especially polypropylene, high density polyethylene, low density polyethylene and ethylene-vinyl acetate copolymers modified with at least one member selected from acrylic acid, methacrylic acid, crotonic acid, fumaric acid, itaconic acid, maleic anhydride,